# **Electronic Supplementary Information**

# Water decontamination by polyoxometalate-functionalized 3Dprinted hierarchical porous devices

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### 1. Instrumentation

**3D printer:** All the models were printed on a commercial 3D printer (Zortrax M200). The filament is acrylonitrile butadiene styrene (SainSmart ABS filament, uncoloured, 1.75 mm).

**Scanning electron microscopy/ energy dispersive X-ray spectroscopy (SEM-EDX):** The morphology and structure of all samples was investigated via field-emission scanning electron microscopy (SEM, ZEISS 1550VP) with an Oxford Instruments EDX system. Samples were measured at 10 keV acceleration voltage.

**ATR-IR spectroscopy:** ATR-IR spectroscopy was performed on a Bruker Tensor 27 FT-IR spectrophotometer including a Platinum ATR unit.

**Raman:** Raman characterization was performed with a confocal InVia Raman micro spectrometer with a 633 nm laser (Renishaw; each spectrum was taken as the average of three x 10 second accumulations).

**Inductively coupled plasma optical emission spectroscopy (ICP-OES):** The metal content of the aqueous solution samples were determined via inductively coupled plasma optical emission spectroscopy (ICP-OES).

**X-ray photoelectron spectroscopy (XPS):** XPS measurements were performed using monochromatized AI Kα radiation on a PHI Quantera SXM system.

**Contact angle measurements:** Static contact angle measurements were performed using a contact angle goniometer (Contact Angle System OCA, DataPhysics). Drop-volumes of 0.5  $\mu$ L Milli-Q water were used.

**General remarks:** All chemicals were purchased from Sigma Aldrich, ABCR or VWR and were of reagent grade. The chemicals were used without further purification.  $Na_9[\alpha-PW_9O_{34}]$  ·12 H<sub>2</sub>O was prepared according to reference 24 (main text).

#### 2. Experimental

#### 2.1 Hydrolysis of ABS

Polymer modification was performed by partial hydrolysis of the ABS based on previous reports: the ABS plates were immersed in a basic hydrolysis solution containing 55 wt.-% water, 35 wt.-% NaOH and 10 wt.-% 1,4-dioxane. Hydrolysis was performed at 65 °C for periods of 5 to 15 minutes. The ABS plates were removed from the reaction solution, rinsed several times with deionized water, rinsed with aqueous HCI (2 M) to neutralize any basic residues and finally rinsed with deionized water again. The samples were then air-dried. The samples are labelled **ABS-0**, **ABS-5**, **ABS-10**, **ABS-15** to indicate the immersion time in the hydrolysis solution in minutes.

#### 2.2 Immobilization of POM onto hydrolyzed ABS

The ABS-15 plates were immersed in 0.01 mol/L  $Na_9[\alpha-PW_9O_{34}]$  (**{PW**<sub>9</sub>}) aqueous solution for 24 h. The **{PW**<sub>9</sub>}-functionalized ABS plates were recovered, washed with de-ionized water and dried in air (**{PW**<sub>9</sub>}@ABS-15).

#### 2.3 Heavy-metal ion adsorption

Metal ion adsorption was performed by immersing  $\{PW_9\}$ @ABS-15 plates into model polluted water for 12 hours (10 mL, 2.2 mM CoCl<sub>2</sub> x 6 H<sub>2</sub>O aqueous solution; 10 mL, 2.2 mM NiCl<sub>2</sub> x 6 H<sub>2</sub>O aqueous solution; 10 mL, 2.2 mM CuSO<sub>4</sub> x 2 H<sub>2</sub>O aqueous solution, respectively). The  $\{PW_9\}$ @ABS-15 plates were recovered, washed with de-ionized water and dried in air, followed by characterization using SEM, EDX, Raman, XPS, contact angles. The residual heavy metal content in the aqueous phase was determined by ICP-OES.

#### 3. Materials and Characterization



**Scheme S1**. Chemical structure of **ABS** resin (based on : Hitachi High-Tech Science Corporation, Application Brief, Thermal Decomposition Measurement of ABS resin I, TA No. 66, Mar. 1995.)



Scheme S2. 3D CAD model of the 3D printed ABS plate and photograph of the ABS plate.

#### 3.1. XPS spectroscopy



Figure S1. XPS survey spectrum of **{PW<sub>9</sub>}@ABS-15**, with inset atomic concentration table.



Figure S2. XPS deconvoluted O 1s spectrum of ABS-15.

## 3.2. SEM-EDX analysis



**Figure S3**. a) SEM image of Ni<sup>2+</sup> adsorbed on **{PW<sub>9</sub>}@ABS-15**; EDX elemental mapping of b) layered image; d) P; e) W; f) Ni; c) EDX spectrum of the whole area of a)



**Figure S4**. a) SEM image of Cu<sup>2+</sup> adsorption by **{PW<sub>9</sub>}@ABS-15**; EDX elemental mapping of b) layered image; d) P; e) W; f) Cu; c) EDX spectrum of the whole area of a)



**Figure S5**. Adsorption of **{PW<sub>9</sub>}** by **ABS-15** plates monitored by UV-Vis spectrometry. The adsorbed amount corresponds to approx. 0.12  $\mu$ mol/mm<sup>2</sup> (for **ABS-5**) and 0.19  $\mu$ mol/mm<sup>2</sup> (for **ABS-15**), based on geometric surface area.